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The electric dipole moment of HD^+ molecular ion

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For the calculations of many molecular properties it is necessary to know their dipole moments. For neutral molecules there has been considerable work, both experimental and theoretical, for the determination of dipole moments. However, for the molecular ions no experimental work and very little theoretical work has been done. Recently in connection with the theoretical study of the collision-induced dissociation of HD^+ ion by electron impact, Saha *et al* (1972) have made an approximate calculation of the dipole moment of HD^+ ion. However, for the calculation of properties which depend more directly on the dipole moment, it is necessary to have accurate value of the latter. In this note the dipole moment of HD^+ molecular ion has been calculated on a more rigorous basis than hitherto done.

The electric dipole moment operator of HD^+ ion can be written as

$$\begin{aligned} \boldsymbol{\rho} &= \Sigma\, e_i \boldsymbol{r}_i, \\ &= -e\boldsymbol{r} + e\boldsymbol{R}_H + e\boldsymbol{R}_D, \\ &= -e\boldsymbol{r} + e\,\frac{M_H - M_D}{M_H + M_D}\,\boldsymbol{R}, \end{aligned} \qquad \ldots\ (1)$$

where e is the protonic charge; $\boldsymbol{r}$, $\boldsymbol{R}_H$ and $\boldsymbol{R}_D$ are the vector distances of the electron, the nuclei H and D respectively, from the centre of mass of the ion (figure 1), M_H and M_D are the masses of the nuclei H and D respectively, and $\boldsymbol{R}$ is the internuclear distance directed from H to D.

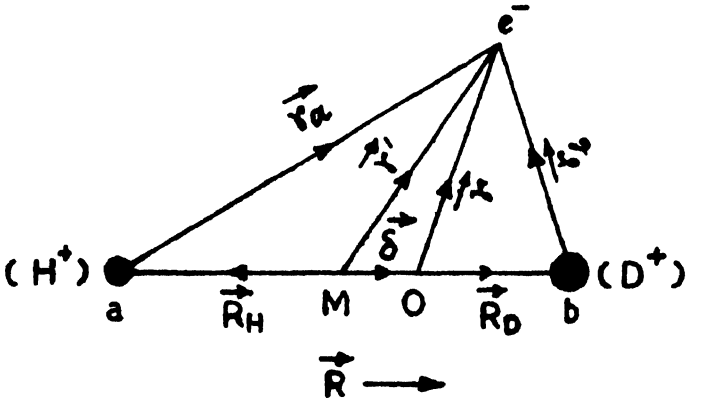

Figure 1. Coordinate system describing the position vectors of the electron and the nuclei of HD^+ ion. a and b specify the nuclei H^+ and D^+ respectively, while e^- the electron. $\vec{R}$ is the internuclear distance directed from a to b. M is the midpoint of the internuclear distance and O is the centre of mass of the molecular ion. $\vec{\delta}$ is the vector displacement of O from M.

The dipole moment in the ground state is given by

$$D = \int \Psi_0^*(\boldsymbol{r}, \boldsymbol{R}) \rho \Psi_0(\boldsymbol{r}, \boldsymbol{R}) d\boldsymbol{r} d\boldsymbol{R}. \quad \ldots (2)$$

$\Psi_0(\boldsymbol{r}, \boldsymbol{R})$ is the ground state wave function of the molecular ion which may be written, by assuming the Born-Oppenheimer separation, as

$$\begin{aligned} \Psi_0(\boldsymbol{r}, \boldsymbol{R}) &= \psi_0(\boldsymbol{r}, R) \xi^v_{JM_J}(\boldsymbol{R}), \\ &= \psi_0(\boldsymbol{r}, R) Y_{JM_J}(\Theta, \Phi) \chi_v(R), \end{aligned} \quad (3)$$

where ψ and ξ represent the electronic and nuclear parts of the wavefunction, Y and χ describe the rotation and the vibration of the ion respectively.

The ground state wave function $\psi_0(\boldsymbol{r}, R)$ may be approximately represented as

$$\psi_0(\boldsymbol{r}, R) = A(R)\{\phi_0(r_a) + \phi_0(r_b)\}, \quad \ldots (4)$$

where r_a and r_b are the distances of the electron from the nuclei $a(H^+)$ and $b(D^+)$ respectively, $\phi_0(r)$ is the hydrogen-like wave function given by (in atomic units)

$$\phi_0(r) = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} \exp(-Zr), \quad \ldots (5)$$

Z being the effective nuclear charge of the HD^+ ion and $A(R)$ the normalisation constant :

$$A(R) = \left[2\left\{1 + \exp(-ZR)\left(1 + ZR + \frac{Z^2R^2}{3}\right)\right\}\right]^{-\frac{1}{2}}. \quad \ldots (6)$$

Then, we get (in a.u.),

$$\boldsymbol{D} = -\int \psi_0^*(\boldsymbol{r}, R)\boldsymbol{r}\,\psi_0(\boldsymbol{r}, R)\xi^{v*}_{JM_J}(\boldsymbol{R})\xi^{v}_{JM_J}(\boldsymbol{R})d\boldsymbol{r}d\boldsymbol{R}$$

$$+\frac{M_H - M_D}{M_H + M_D}\int \psi_0^*(\boldsymbol{r}, R)\psi_0(\boldsymbol{r}, R)\xi^{v*}_{JM_J}(\boldsymbol{R})\boldsymbol{R}\xi^{v}_{JM_J}(\boldsymbol{R})d\boldsymbol{r}d\boldsymbol{R}. \quad \ldots (7)$$

Due to symmetry of the electronic wave function $\psi_0(\boldsymbol{r}, R)$ about an axis passing through the mid-point of the internuclear distance and perpendicular to the internuclear axis, we have,

$$\int \psi_0^*(\boldsymbol{r}', R)\boldsymbol{r}'\psi_0(\boldsymbol{r}', R)d\boldsymbol{r}' = 0. \quad \ldots (8)$$

where $\boldsymbol{r}'$ is the position vector of the electron from the mid-point of the internuclear distance.

Since,

$$\boldsymbol{r} = \boldsymbol{r}' - \boldsymbol{\delta},$$

$$\boldsymbol{\delta} = \frac{1}{2}\frac{M_D - M_H}{M_D + M_H}\boldsymbol{R}. \quad \ldots (9)$$

where $\boldsymbol{\delta}$ is the displacement vector of the centre of mass of the molecular ion from the mid-point of the internuclear distance and $\psi_0(\boldsymbol{r}, R)$ or $\psi_0(\boldsymbol{r}', R)$ is normalised, we get from eqs. (7), (8) and (9),

$$\boldsymbol{D} = -\frac{1}{2}\frac{M_D - M_H}{M_D + M_H}\int \xi^{v*}_{JM_J}(\boldsymbol{R})\boldsymbol{R}\xi^{v}_{JM_J}(\boldsymbol{R})d\boldsymbol{R}$$

$$= -\frac{1}{2}\frac{M_D - M_H}{M_D + M_H}\int \chi_v^*(R)\boldsymbol{R}\chi_v(R)\,Y^*_{JM_J}(\Theta, \Phi)\,Y_{JM_J}(\Theta, \Phi)R^2dR\sin\Theta d\Theta d\Phi. \quad \ldots (10)$$

If we take the z-axis along $\boldsymbol{R}$, then from eq. (10), we get,

$$D_x = D_y = 0,$$

and

$$D_z = D = -\frac{1}{2}\frac{M_D - M_H}{M_D + M_H}\int_0^\infty \chi_v^*(R)R\chi_v(R)R^2dR \quad \ldots (11)$$

since $Y_{JM_J}(\Theta, \Phi)$ is normalised.

Since $M_D > M_H$, eq. (11) reveals that the dipole moment vector of HD^+ ion is directed opposite to $\boldsymbol{R}$ i.e., from the nucleus D to the nucleus H as was shown by Barua *et al* (1971).

For the ground vibrational state, eq. (11) gives us the magnitude of the dipole moment as,

$$D = \frac{1}{2}\frac{M_D - M_H}{M_D + M_H}\int_0^\infty \chi_0^*(R)\chi_0(R)R^3dR \quad \ldots (12)$$

We have taken $\chi_0(R)$ as

$$\chi_0(R) = N_0 R^\lambda \exp(-\alpha R), \qquad \ldots (13)$$

with

$$N_0 = \frac{(2\alpha)^{\lambda+3/2}}{[(2\lambda+2)!]^{\frac{1}{2}}},$$

$$\lambda = -\tfrac{1}{2} + \tfrac{1}{2}(1+4b)^{\frac{1}{2}},$$

$$\alpha = \frac{b}{R_e(\lambda+1)},$$

and

$$b = 4\pi^2 M^2 \nu_0^2 R_e^4 \qquad \ldots (14)$$

in a.u., where ν_0 is the frequency for the ground vibrational state. R_e is the equilibrium internuclear distance and M is the reduced mass of the molecular ion.

Then from eqs. (12) and (13), we get,

$$D = \tfrac{1}{2}\frac{M_D - M_H}{M_D + M_H} N_0^2 \int_0^\infty R^{2\lambda+3} \exp(-2\alpha R) dR,$$

$$= \tfrac{1}{2}\frac{M_D - M_H}{M_D + M_H} N_0^2 \frac{(2\lambda+3)!}{(2\alpha)^{2\lambda+4}},$$

$$= \tfrac{1}{2}\frac{M_D - M_H}{M_D + M_H}\frac{2\lambda+3}{2\alpha}. \qquad \ldots (15)$$

For HD^+ ion, the basic constants are, in a.u. $\nu_0 = 14106 \times 10^{-7}$, $M = 1228$ and $R_e = 2{\cdot}00$ which yield a value of $D = 0{\cdot}34$ a.u. (0·86 Debye) which is somewhat smaller than the value of $D = 0{\cdot}43$ a.u. (1·10 Debye) obtained earlier by Saha *et al* (1972) by neglecting the contribution of the electronic part of the dipole moment operator. The value of D obtained in this note may be further refined by considering the ionic nature of the electronic wavefunction the effect of which is likely to be small for a homopolar molecular ion like HD^+.

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